(12) UK Patent Application (19) GB (11) 2 148 920 A

(43) Application published 5 Jun 1985

(21) Application No 8328584

(22) Date of filing 26 Oct 1983

(51) INT CL⁴
C09B 29/44 D06P 1/18 1/39

(52) Domestic classification
C4P 126 1A3A 1A3B 1C3 1D3 1F1 1F2 1F4 1F5 1F6 1H1Y 1H2 1H3 2G2AY 2H10 2H3 2H4
C2C 1534 213 246 247 250 251 25Y 305 30Y 776 AA ZH
U1S 1565 C2C C4P

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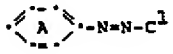
(56) Documents cited
GB 1425205 GB 0327394
"Colour Index" third edition 1971 Society of Dyers and Colourists Volume 4 pages 4041 4042 and 4135 (C.I. No's 12790 12795 19360)

(58) Field of search
C4P

(54) Disperse and acid azo dyes from phenylamines and 1,2-dihydroquinoline couplers

(57) New disperse and acid azo dyes giving bright, green to blue shades having good fastness and non-red flaring on polyamide fibres, have the formula



wherein: ring A is unsubstituted or substituted and C^1 is a 1,2-dihydroquinoline coupler which may be substituted.

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Formulae in the printed specification were reproduced from drawings submitted after the date of filing, in accordance with Rule 20(14) of the Patents Rules 1982.

SPECIFICATION

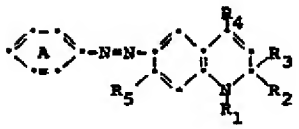
Disperse and acid azo dyes from phenylamines and 1,2-Dihydroquinoline couplers

This invention concerns disperse and acid dyes particularly suited for the dyeing of polyamide fibres, and having the general formula

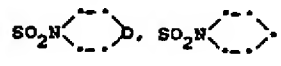
$$D - N = N - C^1$$

wherein D is phenyl, which may be substituted and C^1 is a 1,2-dihydroquinoline coupler which may be substituted preferably in any of the 1, 2, 4 and 7 positions.

Preferably the dyes correspond to the formula



wherein: ring A is unsubstituted for substituted with 1–3 substituents independently selected from alkyl, alkoxy, halogen, trifluoromethyl, thiocyano, cyano, phenylazo, formyl, alkanoyl, alkanoylamino, aroyl, arylsulfonyl, carbamoyl, alkylcarbamoyl, dialkylcarbamoyl, sulfamoyl, alkylsulfamoyl, dialkyl-sulfamoyl, alkylsulfonyl, alkylthio, arylthio, alkyl-SO_3M, aryloxy, alkoxycarbonyl, alkoxy-carbonyloxy, acylamido, aryloxycarbonyl,



alkyl;

R_1 is H, alkyl, aryl or cyclohexyl, wherein said alkyl, aryl and cyclohexyl groups are unsubstituted or substituted with 1–3 substituents different from the parent group and independently selected from hydroxy, alkyl, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C_4H_3O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, $SO_2NHalkyl$, SO_2N-(alkyl)$_2$, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido ($C_4H_4O_2N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), alkyl-SO_3M, cyano, $CONH_2$, CONHalkyl, CON(alkyl)$_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl;

$R_2 - R_3$ are each independently selected from H and alkyl;

R_4 is H, alkyl or alkyl-SO_3M; and

R_5 is selected from H, alkyl, alkoxy, alkenyl of 2–8 carbons, halogen, acylamido, alkylthio and formamido, wherein the alkyl moieties thereof may be substituted with 1–3 substituents independently selected from hydroxy, halogen, cyano, alkoxy, alkyl-SO_3M, alkylthio, alkanoyl, alkanoyloxy, and alkoxycarbonyl;

M is selected from H, Na, K, NH_4, $\frac{Ca}{2}$ $\frac{Zn}{2}$

and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines;

all of the alkyl and cyclic moities in the defined A ring substitients may bear 1–3 substituents different from the parent moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, aryloxy, cyclohexyl, furyl (C_4H_3O), aroyloxy, alkoxycarbonyl, alkoxycarbonyloxy, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, $SO_2NHalkyl$, $SO_2N(alkyl)_2$, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido ($C_4H_4O_4N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), alkyl-SO_3M, 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, CON(alkyl)$_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl.

The various alkyl and alkylene moieties in, for example, alkoxy, alkanoyl and the like within the above definitions of $R_1 - R_5$, and the A ring substituents have 1–6 carbons, and they and the alkenyl groups are straight or branched chain.

Preferred of the above dyes are where ring A is unsubstituted or substituted with 1–3 substituents independently selected from acyl, alkylsulfonyl, alkyl-SO_3M, acylamido, alkyl, carboalkoxy, halogen and cyano, R_1 is hydrogen, alkyl, aryl, cyclohexyl, or said alkyl or cyclohexyl substituted with 1–3 substituents independently selected from halogen, cyano, hydroxy and aryl, and R_5 is hydrogen, alkyl or acylamido.

The dyes of this invention impart blue to green shades on fibers, particularly polyamides, exhibiting improvements in one or more properties such as fastness to light, ozone, perspiration,

oxides of nitrogen, washing, sublimation or crocking, leveling, transfer, pH stability, exhaustion, build and diminished red flaring.

The diazo components used in this invention are prepared according to procedures well known to the art. The present disperse dyes may be applied to polyamide fibers by conventional dyeing procedures, e.g., dispersed in a lignin sulfonate and dyed at 98°C. on nylon fabric for one hour from an aqueous bath. The following examples illustrate procedures which are generally applicable for preparation of the present couplers and dyes.

The acid dyes of the invention may be applied to polyamide fiber by the following method:

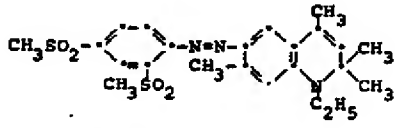
The test dye, as a mixture with a sulphate such as ammonium sulfate, is pasted with boiling water and then made up to a known volume with water to give a weight ratio of water to dye of 30:1. Four percent on weight of fiber (owf) of a lignin sulphonate leveling agent is added, followed by ammonium acetate (about 3.0% owf) to adjust the pH to 6. The initial dyeing temperature is 40°C. which is raised to the final dyeing temperature of 98°C. over 30 minutes. The dye bath is held at 98°C. for 60 minutes, then cooled, and the test fabric given a warm water rinse and air drying.

EXAMPLE 1

(a)– Procedure For the Preparation of 1,2-Dihydro-2,2,4,7-Tetramethylquinoline

Meta-toluidine (535 g.) and iodine (6 g.) are charged to a 2 liter, 3 neck, round bottom flask. The reaction is heated to 155°C. and about 3,500 g. of acetone is added at 155–160°C. beneath the surface over a 12 hour period. A mixture of acetone and water distills off during the addition. The reaction mixture is heated one-half hour at 160°C. and then distilled to about 690 g. of 1,2-dihydro-2,2,4,7-tetramethylquinoline boiling at 107–111°C. at 0.55 mm., a 74% yield. The product is then ethylated with triethylphosphate in the presence of ethyl iodide in known manner.

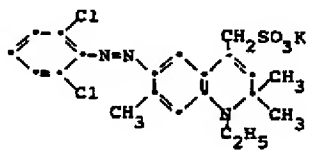
(b) Sodium nitrite (0.72 g.) is added portionwise to 5 ml. of concentrated sulfuric acid. The solution is cooled and 10 ml. of 1:5 acid is added below 15°C. The mixture is cooled further and 2.5 g. 2,4-bis-(methylsulfonyl)aniline is added followed by 10 ml. of 1:5 acid, all below 5°C. After stirring for 2 hours at 0–5°C., the diazonium solution is added to a chilled solution of 3.16 g. of N-ethyl-1,2-dihydro-2,2,4,7-tetramethylquinoline in 50 ml. of 1:5 acid below 5°C. The reaction is kept cold and ammonium acetate added until the coupling mixture is neutral to Congo red test paper. After allowing to couple for 1 hour at about 5°C., the reaction mixture is drowned in water and the product collected by filtration, washed with water, and dried in air. The azo compound obtained gives dyeings having excellent fastness properties on polyamide fibers and has the structure:



The preparation of the sulfonated 1,2-hydroquinoline is given in German Offen. 3,0005,874 (C.A. *94*, 15593K, 1981) and H_2SO_4, $ClSO_3H$, and/or SO_3 and converting, if desired, the acid group to its salt in known manner.

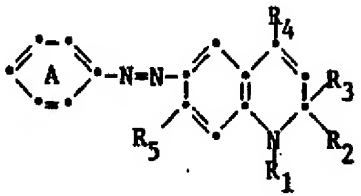
EXAMPLE 2

2,6-Dichloroaniline (0.01 mole) is added to 60% aqueous acetic acid (25.0 cc), with stirring, followed by concentrated sulphuric acid (2.0 cc.). The mixture is cooled to 0°C. Sodium nitrite (0.72 g.), 0.0104 mole) is added to concentrated sulphuric acid (9.2 cc.) and the solution heated to 70°C., for 5 minutes. On cooling to 0°C. the solution is added slowly to the above amine mixture, at 0–5°C. After stirring at 0–5°C. for a further one hour, the diazo solution is added to the potassium salt of 1-ethyl-2,2,7-trimethyl-1,2-dihydroquinolin-4-yl-methyl sulphonic acid (3.33 g., 0.01 mole), in water (11.0 cc.) at <5°C. After stirring at 0–5°C. for one hour the dye is warmed to room temperature and precipitated by adding to saturated potassium chloride solution. The product is filtered and washed with diethyl ether to give the final dye product



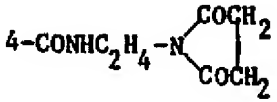
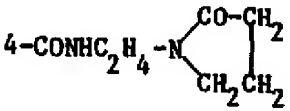
The following table further shows specific dyes of the present invention which are prepared as above.

TABLE 1

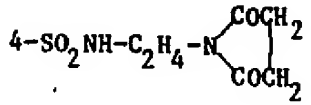
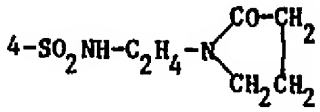


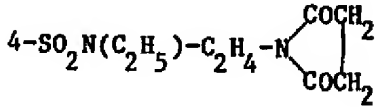
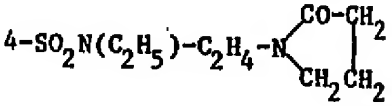
Substituents on Ring A	R_5	R_2	R_3	R_4	R_1
None	H	H	H	H	H
4-CH_2SO_3K	H	H	CH_3	CH_3	C_2H_5
4-Cl	CH_3	CH_3	CH_3	CH_3	C_2H_5
2,5-di-Cl	CH_2CH_2OH	CH_3	CH_3	CH_3	C_2H_5
2,4-di-Cl	CH_2Cl	H	$CH(CH_3)_2$	CH_3	C_2H_5
2-CH_3-5-Cl	OCH_2Cl	H	CH_3	CH_3	C_2H_5
2,5-di-CH_3	OCH_3	H	CH_3	CH_2SO_3K	CH_3
2-CH_3	OCH_3	H	CH_3	H	C_6H_5
4-CH_3	CH_2CH_2CN	H	CH_3	H	C_6H_{11}
3,4-di-CH_3	Cl	H	CH_3	CH_3	C_2H_5
2-Cl-4-SO_2CH_3	Cl	H	CH_3	CH_3	CH_2CH_2OH

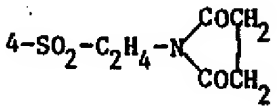
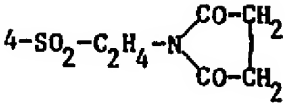
2-Br-4-SO_2CH_3	CH_2SO_3K	H	CH_3	CH_3	CH_2CH_2OH
2-I-4-SO_3CH_3	OCH_3	C_2H_5	C_2H_5	C_2H_5	CH_2CH_2OH
2-Cl-4-SO_2CH_3	NHCHO	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
4-$CO_2C_2H_4$-OH	$NHCOCH_2OCCH_3$	CH_3	CH_3	CH_3	CH_2CN
4-$CO_2C_2H_4$-Cl	$NHCOCH_2CH_3$	CH_3	CH_3	CH_2SO_3Na	CH_2CONH_2
4-$CO_2C_2H_4$-C_6H_{11}	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	H	$CH_2CONHCH_3$
4-$CO_2C_2H_4$-OCH_3	$NHCOC_6H_5$	CH_3	CH_3	CH_2SO_3K	$CH_2CON(C_2H_5)_2$
4-$CO_2C_2H_4$-OC_6H_5	$NHCOC_2H_5$	C_4H_9-n	C_4H_9-n	H	$CH_2NHCOCH_3$
4-$CO_2C_2H_4$-CN	$NHCOC_6H_{11}$	CH_3	CH_3	H	$CH_2NHCOOCH_3$
4-$CO_2C_2H_4$-$OC_2H_4OC_2H_5$	H	CH_3	CH_3	H	CH_2OOCCH_3
4-$CO_2C_2H_4$-$OCOCH_3$	CH_2SCH_3	H	CH_3	H	$CH_2(C_4H_6ON)$
4-$CONHC_2H_4$-SC_6H_5	$CH_2CH{=}CH_2$	H	H	CH_2SO_3N H (Et)$_3$	$CH_2CH_2COOCH_3$
4-$CONHC_2H_4$-Cl	Br	H	CH_3	CH_3	$CH_2CH_2COOCH_3$
4-$CONHC_2H_4$-C_6H_5	I	H	CH_3	CH_3	H
4-$CONHC_2H_4$-C_6H_{11}	F	H	CH_3	CH_3	C_2H_5
4-$CONHC_2H_4$-$OOCCH_3$	SCH_3	H	CH_3	CH_3	C_2H_5
4-$CONHC_2H_4$-SCH_3	CH_2OOCCH_3	H	H	$CH_2CH_2SO_3K$	C_2H_5

4-CONHC$_2$H$_4$-NHCOCH$_3$	OCH$_3$	H	CH$_3$	CH$_3$	C$_2$H$_5$
4-CONHC$_2$H$_4$-CN	CH$_3$	H	CH$_3$	CH$_3$	C$_2$H$_5$
4-CONHC$_2$H$_4$-OC$_2$H$_4$OC$_2$H$_5$	CH$_3$	H	CH$_3$	CH$_3$	CH$_3$
4-CONHC$_2$H$_4$-OCOCH$_3$	CH$_2$CH$_2$COOCH$_3$	C$_2$H$_5$	C$_2$H$_5$	CH$_3$	C$_6$H$_5$
	CH$_2$CH(OH)CH$_2$OH	C$_2$H$_5$	C$_2$H$_5$	CH$_2$SO$_3$(Ca/2)	C$_6$H$_{11}$
4-CONHC$_2$H$_4$-NHSO$_2$C$_2$H$_5$	CF$_3$	C$_2$H$_5$	C$_2$H$_5$	CH$_3$	C$_2$H$_5$
	CF$_3$	H	CH$_3$	CH$_2$SO$_3$(Zn/2)	CH$_2$CH$_2$OH
5-CON(C$_2$H$_5$)-C$_2$H$_4$-SO$_3$K	H	CH$_3$	CH$_3$	CH$_3$	CH$_2$CH$_2$OH
4-CON(C$_2$H$_5$)-C$_2$H$_4$-OH	H	CH$_3$	CH$_3$	CH$_3$	CH$_2$CH$_2$OH
4-CON(C$_2$H$_5$)-C$_2$H$_4$-SC$_6$H$_5$	CH$_2$CH(Cl)CH$_2$Cl	CH$_3$	CH$_3$	CH$_3$	CH$_2$CH$_2$OC$_2$H$_5$
4-CON(C$_2$H$_5$)-C$_2$H$_4$-Cl	CH$_2$CH(OCH$_3$)CH$_2$OCH$_3$	CH$_3$	CH$_3$	CH$_3$	CH$_2$CN
4-CON(C$_2$H$_5$)-C$_2$H$_4$-C$_6$H$_5$	CH$_3$	CH$_3$	CH$_3$	CH$_2$SO$_3$K	CH$_2$CONH$_2$
4-CON(C$_2$H$_5$)-C$_2$H$_4$-OOCCH$_3$	CH$_3$	CH$_3$	CH$_3$	CH$_3$	CH$_2$CONHCH$_3$
4-CON(C$_2$H$_5$)-C$_2$H$_4$-C$_6$H$_{10}$-p-SO$_3$K	CH$_3$	CH$_3$	CH$_3$	CH$_3$	CH$_2$CON(C$_2$H$_5$)$_2$
4-CON(C$_2$H$_5$)-C$_2$H$_4$-OCH$_3$	CH$_3$	CH$_3$	CH$_3$	CH$_3$	CH$_2$NHCOCH$_3$

4-CON(C_2H_5)-C_2H_4-SCH_3	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOOCH_3$
4-CON(C_2H_5)-C_2H_4-OC_6H_5	CH_3	CH_3	CH_3	CH_3	CH_2OOCCH_3
4-CON(C_2H_5)-C_2H_4-$NHCOCH_3$	H	CH_3	CH_3	CH_3	$CH_2(C_4H_6ON)$
4-CON(C_2H_5)-C_2H_4-CN	H	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
4-CON(C_2H_5)-C_2H_4-$OC_2H_4OCH_3$	CH_3	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
4-CON(C_2H_5)-C_2H_4-$OCOCH_3$	CH_2CH_2OH	H	H	C_3H_7-n	H
4-CON(C_2H_5)-C_2H_4-N(COCH$_2$)(COCH$_2$)	CH_2Cl	CH_3	CH_3	C_3H_7-n	C_2H_5
4-CON(C_2H_5)-C_2H_4-$NHSO_2C_2H_5$	OCH_2Cl	CH_3	CH_3	C_2H_5	C_2H_5
4-CON(C_2H_5)-C_2H_4-N(CO-CH$_2$)(CH$_2$CH$_2$)	OCH_3	H	$CH(CH_3)_2$	C_2H_5	C_2H_5
4-$SO_2NHC_2H_5$	OCH_3	H	CH_3	C_2H_5	C_2H_5
4-SO_2NH-C_2H_4-SC_6H_4-p-CH_2SO_3K	CH_2CH_2CN	H	CH_3	CH_3	C_2H_5
4-SO_2NH-C_2H_4-Cl	Cl	H	CH_3	$CH_2SO_3NH(CH_2CH_2OH)_2$	CH_3
4-$SO_2NHC_2H_4$-C_6H_{11}	Cl	H	CH_3	CH_3	C_6H_5
4-SO_2NH-C_2H_4-$OOCCH_3$	H	H	CH_3	CH_3	C_6H_{11}
4-SO_2NH-C_2H_4-OCH_3	OCH_3	H	CH_3	CH_3	C_2H_5

4-$SO_2NH-C_2H_4-SC_2H_5$	NHCHO	H	CH_3	CH_3	CH_2CH_2OH
4-$SO_2NH-C_2H_4-NHCOCH_3$	$NHCOCH_2OCCH_3$	C_2H_5	C_2H_5	CH_3	CH_2CH_2OH
4-$SO_2NHC_2H_4-CN$	$NHCOCH_2CH_3$	CH_3	CH_3	CH_3	CH_2CH_2OH
4-$SO_2NH-C_2H_4-OC_2H_4OCH_3$	$NHCOC_2H_5$	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
4-$SO_2NH-C_2H_4-OCOCH_3$	$NHCOC_6H_5$	CH_3	CH_3	CH_3	CH_2CN
	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	CH_3	CH_2CONH_2
4-$SO_2NH-C_2H_4-NHSO_2C_2H_5$	H	H	H	CH_2SO_3Na	H
	H	H	CH_3	$CH_2SO_3NH_4$	C_2H_5
4-$SO_2N(C_2H_5)C_2H_5$	CH_3	CH_3	CH_3	CH_3	C_2H_5
4-$SO_2N(C_2H_5)-C_2H_4-OH$	CH_2CH_2OH	CH_3	CH_3	$CH_2CH_2SO_3H$	C_2H_5
4-$SO_2N(C_2H_5)-C_2H_4-SC_6H_5$	CH_2Cl	H	$CH(CH_3)_2$	CH_3	C_2H_5
4-$SO_2N(C_2H_5)-C_2H_4-Cl$	OCH_2Cl	H	CH_3	CH_3	C_2H_5
4-$SO_2N(C_2H_5)-C_2H_4-OOCCH_3$	OCH_3	H	CH_3	H	CH_3
4-$SO_2N(C_2H_5)-C_2H_4-C_6H_{11}$	OCH_3	H	CH_3	H	C_6H_5
4-$SO_2N(C_2H_5)-C_2H_4-C_6H_5$	CH_2CH_2CN	H	CH_3	H	C_6H_{11}

4-$SO_2N(C_2H_5)-C_2H_4-OCH_3$	Cl	H	CH_3	CH_3	C_2H_5
4-$SO_2N(C_2H_5)-C_2H_4-SCH_3$	Cl	H	CH_3	CH_3	CH_2CH_2OH
4-$SO_2N(C_2H_5)-C_2H_4-NHCOCH_3$	H	H	CH_3	CH_3	CH_2CH_2OH
4-$SO_2N(C_2H_4)-C_2H_4-CN$	OCH_3	C_2H_5	C_2H_5	C_2H_5	CH_2CH_2OH
4-$SO_2N(C_2H_5)-C_2H_4-OC_2H_4OCH_3$	NHCHO	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
4-$SO_2N(C_2H_5)-C_2H_4-OCOCH_3$	$NHCOCH_2OCCH_3$	CH_3	CH_3	CH_3	CH_2CN
	$NHCOCH_2CH_3$	CH_3	CH_3	H	CH_2CONH_2
4-$SO_2N(C_2H_5)-C_2H_4-OC_6H_5$	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	H	$CH_2CONHCH_3$
4-$SO_2N(C_2H_5)-C_2H_4-NHSO_2C_2H_5$	$NHCOC_6H_5$	CH_3	CH_3	H	$CH_2CON(C_2H_5)_2$
	$NHCOC_2H_5$	C_4H_9-n	C_4H_9-n	CH_2SO_3H	$CH_2NHCOCH_3$
4-$SO_2C_2H_4$	$NHCOC_6H_{11}$	CH_3	CH_3	H	$CH_2NHCOOCH_3$
4-$SO_2-C_2H_4-OH$	H	CH_3	CH_3	H	CH_2OOCCH_3
4-$SO_2C_2H_4-SC_6H_5$	CH_2SCH_3	H	CH_3	H	$CH_2(C_4H_6ON)$
4-$SO_2-C_2H_4-Cl$	$CH_2CH=CH_2$	H	H	H	$CH_2CH_2COOCH_3$
4-$SO_2-C_2H_4-C_6H_{11}$	Br	H	CH_3	CH_3	$CH_2CH_2COOCH_3$

4-SO_2-C_2H_4-SCH_3	I	H	CH_3	CH_3	H
4-SO_2-C_2H_4-OC_6H_5	F	H	CH_3	CH_3	C_2H_5
4-SO_2-C_2H_4-$NHCOCH_3$	SCH_3	H	CH_3	CH_3	C_2H_5
4-SO_2-C_2H_4-CN	CH_2OOCCH_3	H	H	H	C_2H_5
4-SO_2-C_2H_4-$OC_2H_4OC_2H_5$	OCH_3	H	CH_3	CH_3	C_2H_5
4-SO_2-C_2H_4-$OCOCH_3$	CH_3	H	CH_3	CH_3	C_2H_5
	CH_3	H	CH_3	CH_3	CH_3
4-SO_2-C_2H_4-$NHSO_2C_2H_5$	$CH_2CH_2COOCH_3$	C_2H_5	C_2H_5	CH_3	C_6H_5
	$CH_2CH(OH)CH_2OH$	C_2H_5	C_2H_5	CH_3	C_6H_{11}
2-CN-4-SO_2CH_3	CF_3	C_2H_5	C_2H_5	CH_3	C_2H_5
2-CN-4-Cl	CF_3	H	CH_3	CH_3	CH_2CH_2OH
2-CN-4-$COCH_3$	H	CH_3	CH_3	CH_3	CH_2CH_2OH
2-CN-4-$COOC_2H_5$	H	CH_3	CH_3	CH_3	CH_2CH_2OH
2,4-di-CN	$CH_2CH(Cl)CH_2Cl$	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
4-$SO_2C_6H_5$	$CH_2CH(OCH_3)CH_2OCH_3$	CH_3	CH_3	CH_3	CH_2CN

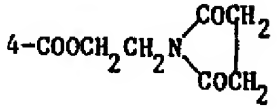
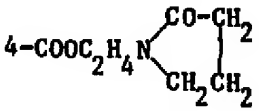
4-SO_2NH_2	CH_3	CH_3	CH_3	CH_3	CH_2CONH_2
4-$SO_2N(C_2H_5)_2$	CH_3	CH_3	CH_3	CH_3	$CH_2CONHCH_3$
2-Cl-5-$SO_2NHC_2H_4OH$	CH_3	CH_3	CH_3	CH_3	$CH_2CON(C_2H_5)_2$
2-Cl-5-SO_2CH_3	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOCH_3$
2,5-di-Cl-4-SO_2N 	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOOCH_3$
2,6-di-Cl-4-SO_2CH_3	CH_3	CH_3	CH_3	CH_3	CH_2OOCCH_3
2,6-di-CN-4-SO_2CH_3	H	CH_3	CH_3	CH_3	$CH_2(C_4H_6ON)$
2,6-di-CN-4-CHO	H	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
2,6-di-CN-4-Cl	CH_3	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
2,6-di-CN-4-$COCH_3$	CH_2CH_2OH	H	H	C_3H_7-n	H
2,6-di-CN-4-$CONHC_2H_5$	CH_2Cl	CH_3	CH_3	C_3H_7-n	C_2H_5
2,6-di-CN-4-$COOC_2H_5$	OCH_2Cl	CH_3	CH_3	C_2H_5	C_2H_5
2-CF_3-4-Br	OCH_3	H	$CH(CH_3)_2$	C_2H_5	C_2H_5
2,5-di-Cl-4-SO_2N 	OCH_3	H	CH_3	C_2H_5	C_2H_5
2-$COOCH_3$-4-SCN	CH_2CH_2CN	H	CH_3	CH_3	C_2H_5

2-SO_2CH_3-4-SCN	Cl	H	CH_3	CH_3	CH_3
2-$COCH_3$-4-SCN	Cl	H	CH_3	CH_3	C_6H_5
2-Br-4-$CONH_2$	H	H	CH_3	CH_3	C_6H_{11}
2-CN-4-$CONH_2$	OCH_3	H	CH_3	CH_3	C_2H_5
2-CN-4-$CONH_2$	NHCHO	H	CH_3	CH_3	CH_2CH_2OH
	$NHCOCH_2OCH_3$	C_2H_5	C_2H_5	CH_3	CH_2CH_2OH
4-COC_6H_5	$NHCOCH_2CH_3$	CH_3	CH_3	CH_3	CH_2CH_2OH
2-$SO_2C_6H_5$	$NHCOC_2H_5$	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
4-$SO_3C_6H_5$	$NHCOC_6H_5$	CH_3	CH_3	CH_3	CH_2CN
2-OCH_3-4,6-di-Cl	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	CH_3	CH_2CONH_2
2-OCH_3-5-CH_3	H	H	H	H	H
4-$NHCOCH_3$	H	H	CH_3	CH_3	C_2H_5
4-NHCOH	CH_3	CH_3	CH_3	CH_3	C_2H_5
2-CN-4-SCN	CH_2CH_2OH	CH_3	CH_3	CH_3	C_2H_5
2,4-di-Br-6-$COOCH_3$	CH_2Cl	H	$CH(CH_3)_2$	CH_3	C_2H_5
2-Br-4-SCN-6-$COOCH_3$	OCH_2Cl	H	CH_3	CH_3	C_2H_5

4-$NHSO_2C_2H_5$	H	CH	H	CH
2-CN-4-SCN-6-$COOCH_3$	OCH_3	H	CH_3	H
2-CN-4,6-di-Cl	CH_2CH_2CN	H	CH_3	H
2,5-di-CN	Cl	H	CH_3	CH_3
2-CN-4-$SO_2C_2H_5$	Cl	H	CH_3	CH_3
3,5-di-$COOCH_3$	H	H	CH_3	CH_3
3,4-di-CN	OCH_3	C_2H_5	C_2H_5	C_2H_5
3,4-di-Cl-2,6-di-CN	NHCHO	CH_3	CH_3	CH_3
2,6-di-Br-4-SO_2CH_3	$NHCOCH_2OCH_3$	CH_3	CH_3	CH_3
2,6-di-Br-4-$SO_2N(CH_3)_2$	$NHCOCH_2CH_3$	CH_3	CH_3	H
2,6-di-Br-4-CHO	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	H
2,6-di-Br-4-$COCH_3$	$NHCOC_6H_5$	CH_3	CH_3	H
2-CN-4-CHO	$NHCOC_2H_5$	C_4H_9-n	C_4H_9-n	H
2-CN-4-$COOCH(CH_3)_2$	$NHCOC_6H_{11}$	CH_3	CH_3	H
2-SO_2CH_3-4-Cl	H	CH_3	CH_3	H
2-SO_2CH_3-4-CN	CH_2SCH_3	H	CH_3	H
2-$COOCH_3$-4-SO_2CH_3	$CH_2CH{=}CH_2$	H	H	H

3	
C_6H_5	
C_6H_{11}	
C_2H_5	
CH_2CH_2OH	
CH_2CH_2OH	
CH_2CH_2OH	
$CH_2CH_2OC_2H_5$	
CH_2CN	
CH_2CONH_2	
$CH_2CONHCH_3$	
$CH_2CON(C_2H_5)_2$	
$CH_2NHCOCH_3$	
$CH_2NHCOOCH_3$	
CH_2OOCCH_3	
$CH_2(C_4H_6ON)$	
$CH_2CH_2COOCH_3$	

2-CONHC$_2$H$_4$OH-4-Cl	Br	H	CH$_3$	CH$_3$	CH$_2$CH$_2$COOCH$_3$
2-Cl-4-SO$_2$CH$_3$	I	H	CH$_3$	CH$_3$	H
2-Cl-4-SO$_2$C$_4$H$_9$-n	F	H	CH$_3$	CH$_3$	C$_2$H$_5$
2-Br-4-COOC$_4$H$_9$-n	SCH$_3$	H	CH$_3$	CH$_3$	C$_2$H$_5$
2,6-di-Br-4-CHO	CH$_2$OOCCH$_3$	H	H	H	C$_2$H$_5$
2,6-di-Cl-4-SO$_2$CH$_3$	OCH$_3$	H	CH$_3$	CH$_3$	C$_2$H$_5$
2-I-4-SO$_2$CH$_3$	CH$_3$	H	CH$_3$	CH$_3$	C$_2$H$_5$
4-CN-2-SC$_2$H$_4$OH	CH$_3$	H	CH$_3$	CH$_3$	CH$_3$
4-CN-2,6-di-SCH$_2$CH$_3$	CH$_2$CH$_2$COOCH$_3$	C$_2$H$_5$	C$_2$H$_5$	CH$_3$	C$_6$H$_5$
4-CN-2-OC$_6$H$_5$	CH$_2$CH(OH)CH$_2$OH	C$_2$H$_5$	C$_2$H$_5$	CH$_3$	C$_6$H$_{11}$
4-CO$_2$C$_6$H$_5$	CF$_3$	C$_2$H$_5$	C$_2$H$_5$	CH$_2$SO$_3$K	C$_2$H$_5$
4-CONHC$_2$H$_4$OH	CF$_3$	H	CH$_3$	CH$_3$	CH$_2$CH$_2$OH
4-CONHC$_3$H$_6$OCH$_3$	H	CH$_3$	CH$_3$	CH$_3$	CH$_2$CH$_2$OH
4-COOCH$_2$CH$_2$C$_6$H$_5$	H	CH$_3$	CH$_3$	CH$_2$SO$_3$NH$_4$	CH$_2$CH$_2$OH
4-SO$_2$NHC$_2$H$_4$Cl	CH$_2$CH(Cl)CH$_2$Cl	CH$_3$	CH$_3$	CH$_3$	CH$_2$CH$_2$OC$_2$H$_5$
4-SO$_2$NHCH$_2$C$_6$H$_{11}$	CH$_2$CH(OCH$_3$)CH$_2$OCH$_3$	CH$_3$	CH$_3$	CH$_2$SO$_3$K	CH$_2$CN
4-CONHC$_2$H$_4$OC$_2$H$_4$CN	CH$_3$	CH$_3$	CH$_3$	CH$_3$	CH$_2$CONH$_2$

4-$CONHC_2H_4OC_6H_5$	CH_3	CH_3	CH_3	CH_3	$CH_2CONHCH_3$
4-SC_6H_5	CH_3	CH_3	CH_3	CH_3	$CH_2CON(C_2H_5)_2$
	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOCH_3$
4-$COOC_2H_4NHCOCH_3$	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOOCH_3$
4-$COOC_2H_4NHSO_2CH_3$	CH_3	CH_3	CH_3	CH_3	CH_2OOCCH_3
	H	CH_3	CH_3	CH_3	$CH_2(C_4H_6ON)$
4-$COOC_2H_4S-CH_3$	H	CH_3	CH_3	CH_2SO_3Na	$CH_2CH_2COOCH_3$
4-$COOC_2H_4S-C_6H_5$	CH_3	CH_3	CH_3	CH_2SO_3K	$CH_2CH_2COOCH_3$
4-$SO_2NHCH_2CH(OH)CH_2OH$	CH_2CH_2OH	H	H	C_3H_7-n	H
4-$SO_2N(CH_3)C_2H_4OH$	CH_2Cl	CH_3	CH_3	C_3H_7-n	C_2H_5
4-$SO_2N(C_2H_5)_2$	OCH_2Cl	CH_3	CH_3	C_2H_5	C_2H_5
4-$SO_2N(CH_3)CH_2CH_2OH$	OCH_3	H	$CH(CH_3)_2$	C_2H_5	C_2H_5
4-$SO_2CH_2CH_2OCOCH_3$	OCH_3	H	CH_3	C_2H_5	C_2H_5
4-$SO_2CH_2CH_2OC_2H_5$	CH_2CH_2CN	H	CH_3	CH_3	C_2H_5
4-$SO_2CH_2CH_2OH$	Cl	H	CH_3	CH_3	CH_3

2,4-di-SO_2CH_3	Cl	H	CH_3	CH_3	C_6H_5
2-Br-4,6-di-SO_2CH_3	H	H	CH_3	CH_3	C_6H_{11}
2-CN-4,6-di-SO_2CH_3	OCH_3	H	CH_3	CH_3	C_2H_5
4-$OCOOCH_3$	NHCHO	H	CH_3	CH_3	CH_2CH_2OH
4-$OCOOCH_2CH_2OCOOCH_3$	$NHCOCH_2OCCH_3$	C_2H_5	C_2H_5	CH_3	CH_2CH_2OH
4-C_2H_4-(C_4H_3O)	$NHCOCH_2CH_3$	CH_3	CH_3	CH_3	CH_2CH_2OH
4-C_6H_4-p-CH_3	$NHCOC_2H_5$	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
4-CH_2CH_2-$OOCC_6H_5$	$NHCOC_6H_5$	CH_3	CH_3	CH_3	CH_2CN
4-CH_2CH_2-SO_2NH_2	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	CH_3	CH_2CONH_2
4-CH_2CH_2-SO_2NHPh	H	H	H	H	H
4-CH_2CH_2-SO_2NHCH_3	H	H	CH_3	CH_3	C_2H_5
4-CH_2CH_2-$SO_2N(C_2H_5)_2$	CH_3	CH_3	CH_3	CH_3	C_2H_5
4-CH_2CH_2-$NHCOOCH_3$	CH_2CH_2OH	CH_3	CH_3	CH_3	C_2H_5
4-CH_2CH_2-$NHCONHCH_3$	CH_2Cl	H	$CH(CH_3)_2$	CH_3	C_2H_5
4-CH_2CH_2-($C_5H_6O_2N$)	OCH_2Cl	H	CH_3	CH_3	C_2H_5
4-CH_2CH_2-($C_8H_4O_2N$)	OCH_3	H	CH_3	CH_2SO_3K	CH_3
4-CH_2CH_2-$CONH_2$	OCH_3	H	CH_3	H	C_6H_5

4-CH_2CH_2-$CONHCH_3$	CH_2CH_2CN	H	CH_3	CH_2SO_3K	C_6H_{11}
4-CH_2CH_2-$CON(CH_3)_2$	Cl	H	CH_3	CH_3	C_2H_5
4-CH_2CH_2-SO_2CH_3	Cl	H	CH_3	CH_3	CH_2CH_2OH
4-CH_2CH_2-SO_2Ph	H	H	CH_3	CH_3	CH_2CH_2OH
4-$COCH_3$	CH_3	CH_3	CH_3	H	C_2H_5
3-Cl	CH_3CONH	CH_3	CH_3	H	C_2H_5
4-Cl,2,6-di-CN	CH_3	CH_3	CH_3	H	C_2H_5
2-CH_3,4-CH_3SO_2	H	H	H	H	C_2H_5
H	H	H	H	H	C_2H_5
4-$COCH_3$	CH_3	CH_3	CH_3	CH_2SO_3K	C_2H_5
3-Cl	CH_3CONH	CH_3	CH_3	CH_2SO_3Na	C_2H_5
4-Cl,2,6-di-CN	CH_3	CH_3	CH_3	CH_2SO_3K	C_2H_5
2,4-di-CH_3SO_2	CH_3	CH_3	CH_3	CH_2SO_3K	C_2H_5
2,CH_3,4-CH_3SO_2	H	H	H	$CH_2SO_3(Ca/2)$	C_2H_5
H	H	H	H	$CH_2SO_3NH_4$	C_2H_5

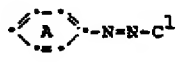
CLAIMS

1. A dye of the general formula:

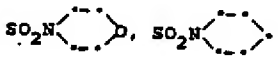
$$D - N = N - C^1$$

wherein D is a phenyl or substituted phenyl group and C^1 is a 1,2-dihydroquinoline coupler which may be substituted.

2. A dye according to Claim 1 of the formula



wherein ring A is unsubstituted or substituted with 1–3 substituents independently selected from alkyl, alkoxy, halogen, trifluoromethyl, thiocyano, cyano, phenylazo, formyl, alkanoyl, alkanoylamino, aroyl, arylsulfonyl, carbamoyl, alkylcarbamoyl, dialkylcarbamoyl, sulfamoyl, alkyl-SO_3M, alkylsulfamoyl, dialkylsulfamoyl, alkylsulfonyl, alkylthio, arylthio, aryloxy, alkoxycarbonyl, alkoxycarbonyloxy, acylamido, aryloxycarbonyl,

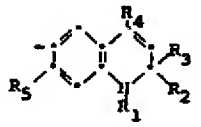


SO_2O-aryl, and $NHSO_2$-alkyl, wherein M is selected from H, Na, K, NH_4,

$$\frac{Ca}{2} \quad \frac{Zn}{2}$$

and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines and wherein all of the alkyl and cyclic moieties in the defined A ring substituents may bear 1–3 substituents different from the parent moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, aryloxy, cyclohexyl, furyl (C_4H_3O), aroyloxy, alkoxycarbonyl, alkoxycarbonyloxy, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, $SO_2NHalkyl$, $SO_2N(alkyl)_2$, alkyl-SO_3M, NHCOOalkyl, NHCON-Halkyl, acylamido, alkyl-sulfonamido, succinimido ($C_4H_4O_2N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxy-alkoxy, alkylthio, and C^1 is a 1,2-dihydroquinoline coupler which is unsubstituted or substituted in any of the 1, 2, 4 and 7 positions.

3. A dye according to Claim 1 or 2 wherein C^1 has the formula



wherein R_1 is H, alkyl, aryl or cyclohexyl, wherein said alkyl, aryl and cyclohexyl groups are unsubstituted or substituted with 1–3 substituents different from the parent group and independently selected from hydroxy, alkyl, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C_4H_3O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, $SO_2NHalkyl$, alkyl-SO_3M, $SO_2N(alkyl)_2$, NHCOOalkyl, NHCONH-alkyl, acylamido, alkylsulfonamido, succinimido ($C_4H_4O_2N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl;

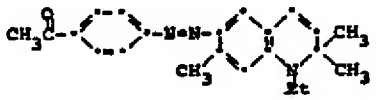
$R_2 - R_3$ are each inependently selected from H and alkyl;

R_4 is H, alkyl or alkyl $- SO_3M$; and

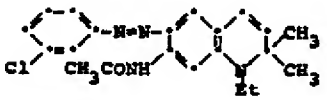
R_5 is selected from H, alkyl, alkoxy, alkenyl of 2–8 carbons, halogen, acylamido, alkylthio and formamido, wherein the alkyl moieties thereof may be substituted with 1–3 substituents independently selected from hydroxy, halogen, cyano, alkoxy, alkylthio, alkanoyl, alkyl-SO_3M, alkanoyloxy, and alkoxycarbonyl.

4. A dye according to Claim 2 wherein ring A is unsubstituted or substituted with 1–3 substituents independently selected from acyl, alkylsulfonyl, alkyl-SO_3M, acylamido, alkyl, carboalkoxy, halogen and cyano, R_1 is hydrogen, alkyl, aryl, cyclohexyl, or said alkyl or cyclohexyl substituted with 1–3 substituents independently selected from halogen, cyano, hydroxy and aryl, and R_5 is hydrogen, alkyl or acylamido.

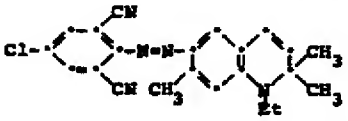
5. The dye according to Claim 1 of the formula



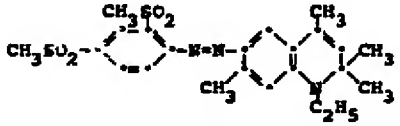
6. The dye according to Claim 1 of the formula



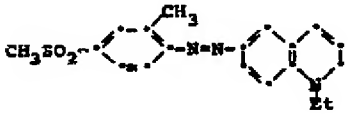
7. The dye according to Claim 1 of the formula



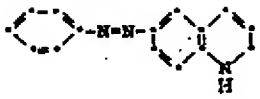
8. The dye according to Claim 1 of the formula



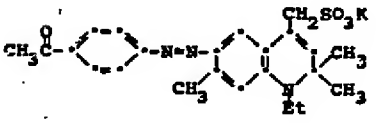
9. The dye according to Claim 1 of the formula



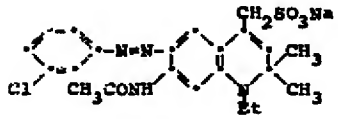
10. The dye according to Claim 1 of the formula



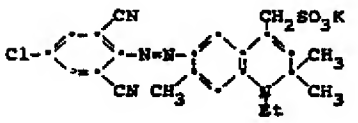
11. The dye according to Claim 1 of the formula



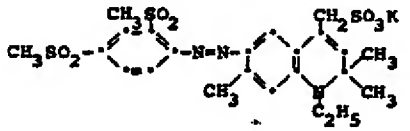
12. The dye according to Claim 1 of the formula



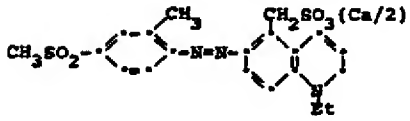
13. The dye according to Claim 1 of the formula



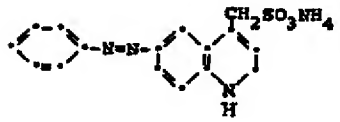
14. The dye according to Claim 1 of the formula



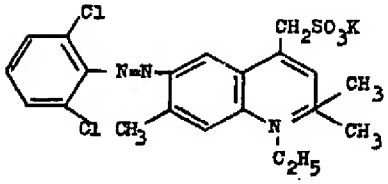
15. The dye according to Claim 1 of the formula



16. The dye according to Claim 1 of the formula



17. The dye according to claim 1 of the formula



Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1985, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.